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STAZIONI SPERIMENTALI PER L'INDUSTRIA

La nuova norma ISO 4259 per la determinazione  
e l'applicazione dei dati di precisione

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## ISO 4259

**ISO 4259**, *Petroleum products - Determination and application of precision data in relation to methods of test*

- Editions: 1979 / 1992 + Cor. 1:1993 / 2006

**ISO 4259-1:2017**, *Petroleum and related products - Precision of measurement methods and results - Part 1: Determination of precision data in relation to methods of test*

**ISO 4259-2:2017**, *Petroleum and related products - Precision of measurement methods and results - Part 2: Interpretation and application of precision data in relation to methods of test*

# ISO 4259

## ISO 4259:2017 (Part 1 and Part 2)

- The committee responsible for this document is **ISO/TC 28**, *Petroleum and related products, fuels and lubricants from natural or synthetic sources*
- This edition cancels and replaces the third edition, ISO 4259:2006, which has been technically revised
- **The two parts encompass both the determination of precision estimates and the application of precision data.** They combine the information in **ASTM D6300** regarding the determination of the precision estimates and the information in **ASTM D3244** for the utilization of test data
- The procedures in this document have been designed specifically for **petroleum and petroleum related products**, which are normally considered as homogeneous. However, the procedures described in this document can also be applied to **other types of homogeneous products**

# ISO 4259

## ISO 4259-1:2017

- This document specifies the methodology for the **design of an Interlaboratory Study (ILS)** and **calculation of precision estimates** of a test method specified by the study. In particular, it defines the relevant **statistical terms**, the procedures to be adopted in the **planning of ILS** to determine the precision of a test method, and the **method of calculating the precision** from the results of such a study
- Calculation of precision estimates over all samples (if this is not possible, then the alternative sample by sample procedures of ISO 5725-2 shall be used)

# ISO 4259

## ISO 4259-1:2017

- The **stages** in planning an interlaboratory study are as follows:
  - preparing a **draft method of test**
  - planning and executing a **pilot study**
  - planning and executing the **interlaboratory study**
- The **draft method of test** shall contain all the necessary details for carrying out the test and reporting the results
- The **pilot study** is necessary to verify the feasibility of the study and to estimate approximately the precision and bias of the test method (at least twelve laboratory/sample combinations shall be included)

# ISO 4259

## ISO 4259-1:2017

### Planning and executing the interlaboratory study

- There shall be **at least 6 participating laboratories**, but it is recommended this number be increased to **8 or more** in order to ensure the **final precision is based on at least 6 laboratories and to ensure the precision statement is more representative of the user population**
- The number of samples shall be sufficient to adequately represent the **types of materials** to which the test method is to be applied, to **cover the range of the property measured** at approximately equidistant intervals, and to **give reliability to the precision estimates**. If precision is found to vary with the level of results in the pilot study, than **at least 5 samples** shall be used in the interlaboratory study

# ISO 4259

## ISO 4259-1:2017

### Planning and executing the interlaboratory study

- In order to correctly estimate precision versus level relationship, it is important that the choice of **samples evenly covers the range and materials for the property measured**, so that an estimated relationship is not too dependent upon the **leverage** of a sample with extreme property value
- It is strongly recommended that the **leverage** of each planned sample in the sample set design is assessed
- Both the material identification and the corresponding duplicate shall be **blinded** such that the tester does not know the material identification of the test sample, nor its corresponding duplicate run

# ISO 4259

## ISO 4259-1:2017

### **Statistical treatment of the results and calculation of precision estimates**

- Pre-screen using GESD technique (Rosner's Outlier Test)
- Transformation of data and outlier tests (Cochran and Hawkins)
- Confirmation of selected transformation and identification of excessively influential samples using Cook's Distance
- Analysis of variance (two-factor with replication)
- Calculation of precision estimates (r & R)



# ISO 4259

## ISO 4259-1:2017

### Evaluation of precision estimates

- In any event, it is necessary to obtain **at least 30 degrees of freedom for both repeatability and reproducibility**
- The working range shall be determined based on lowest and highest achieved non-rejected results from the ILS
  - **Comment: why non-rejected results and not sample means?**
- A large R/r ratio (i.e.  $> 4$ ) is an indication that the laboratory-bias effect is a significantly dominant contributor towards R over the random effects (further standardization of the test method is necessary)

# ISO 4259

## ISO 4259-1:2017

### Specification of scope for the test method - Lower limit

- **The lower limit of the scope of the test method shall be the larger of:**
  - **lowest sample mean** tested in the ILS or
  - **lowest achievable result + 2R**, where R is evaluated at the lowest sample mean. The lowest achievable result is defined as the point of truncation (excluding minus infinity) below which a result is not defined (e.g. 0 point for a percent concentration)
- **Due to testing variation, the lowest acceptable single result that is deemed as a valid result of the test method shall be:**
  - **lower method scope limit - 1,2R**, where R is evaluated at the low method scope limit value

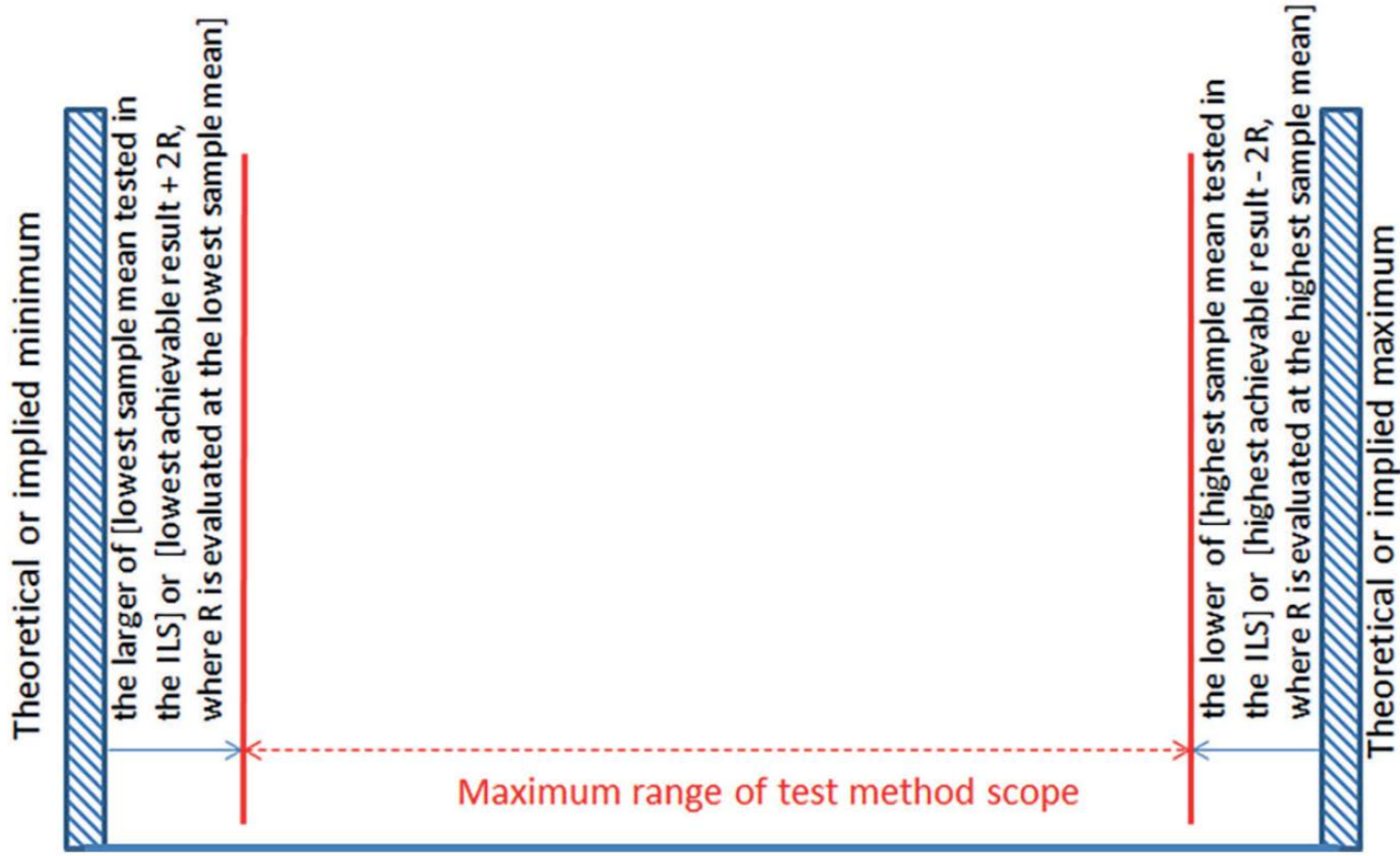
# ISO 4259

## ISO 4259-1:2017

### Specification of scope for the test method - Upper limit

- **The upper limit of the scope of the test method shall be the lesser of:**
  - **highest sample mean** tested in the ILS or
  - **highest achievable result - 2R**, where R is evaluated at the highest sample mean. The highest achievable result is defined as the point of truncation (excluding plus infinity) above which a result is not defined (e.g. 100 point for a percent concentration)
- **Due to testing variation, the highest acceptable single result that is deemed as a valid result of the test method shall be:**
  - **higher method scope limit + 1,2R**, where R is evaluated at the high method scope limit value

# ISO 4259



## ISO 4259

### Example of specification of scope for a test method - Lower limit

Sulfur in automotive fuels by WDXRF - EN ISO 20884:2011 (low range)

- $R = 0,1201 X + 1,9$                       Working range: 5 - 60 mg/kg
- Lower limit of the scope of the test method: 4,5 mg/kg, the larger of:
  - lowest sample mean tested in the ILS: 3 mg/kg
  - lowest achievable result + 2R: 4,5 mg/kg
- Lowest acceptable single result that is deemed as a valid result of the test method: 1,6 mg/kg
- According to the 2006 edition, it is recommended that the lower limit of the scope of the test method is not less than 5,0 mg/kg
- $R(4,5) = 2,4$  (53%)                       $R(5,0) = 2,5$  (50%)

## ISO 4259

### Example of specification of scope for a test method - Lower limit

Sulfur in LPG by UVF - ASTM D6667-14

- $R = 2,3205 X^{0,7}$                       Working range: 1 - 196 mg/kg
- Lower limit of the scope of the test method: 4,6 mg/kg, the larger of:
  - lowest sample mean tested in the ILS: 1 mg/kg
  - lowest achievable result + 2R: 4,6 mg/kg
- Lowest acceptable single result that is deemed as a valid result of the test method: -3,5 mg/kg (!)
- According to the 2006 edition, it is recommended that the lower limit of the scope of the test method is not less than 166,7 mg/kg
- $R(4,6) = 6,8$  (148%)                       $R(166,7) = 83,4$  (50%)

# ISO 4259

## ISO 4259-2:2017

- This document specifies the methodology for the **application of precision estimates of a test method** derived from ISO 4259-1. In particular, it defines the **procedures for setting the property specification limits based upon test method precision** where the property is determined using a specific test method, and in **determining the specification conformance status when there are conflicting results between supplier and receiver**

# ISO 4259

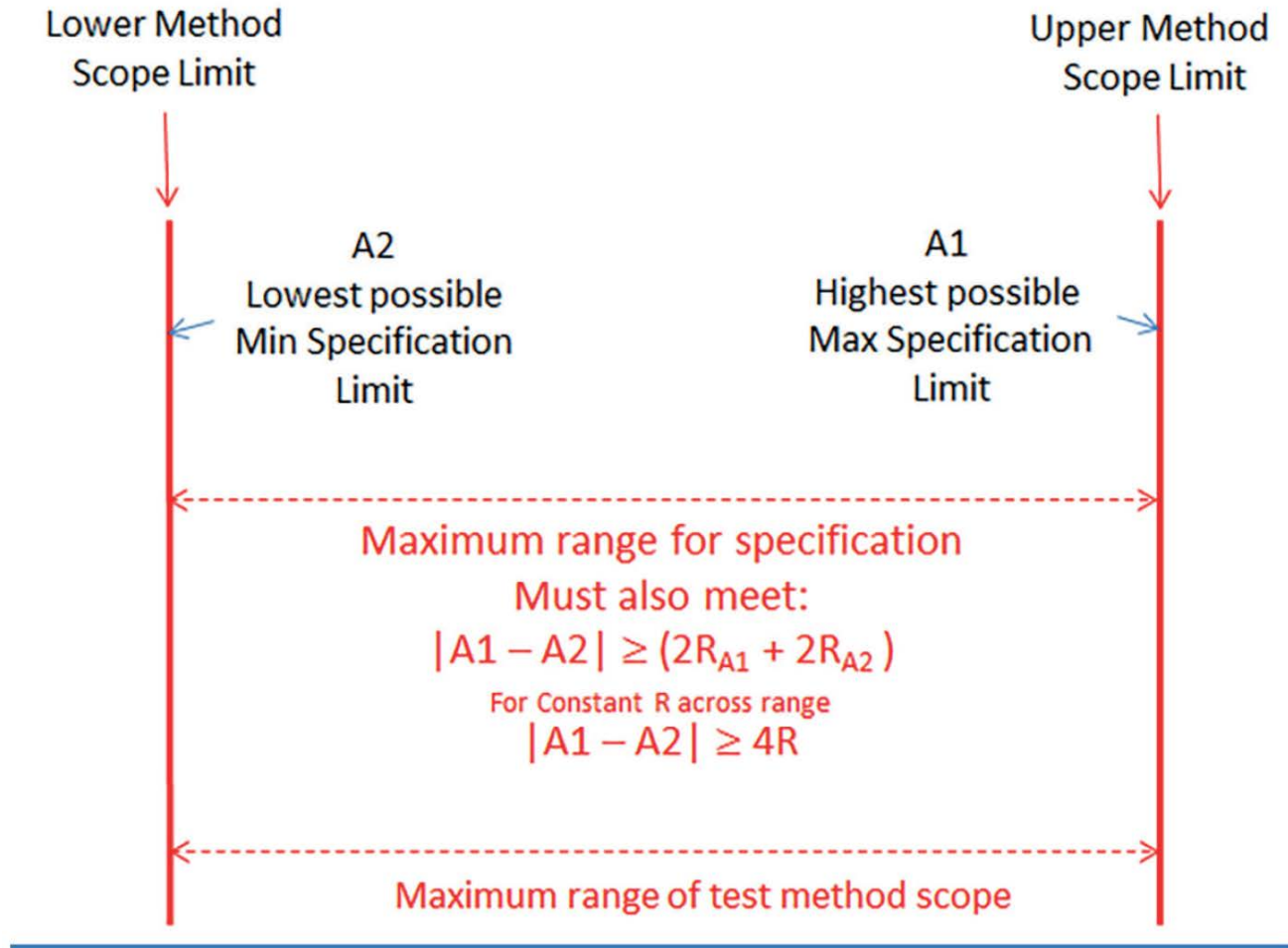
## ISO 4259-2:2017

### Construction of specifications limits in relation to scope and precision of the specified test method

- **The specification limits shall not be outside the method scope limits as determined in ISO 4259-1**
- The lower specification limit shall not be less than the lower scope limit of the test method, and the upper specification limit shall not be greater than the upper scope limit of the test method
- **In addition, the distance between lower and upper specification limit shall also satisfy the following condition: upper specification limit minus lower specification limit shall not be less than the quantity  $2R$  evaluated at lower method scope limit plus  $2R$  evaluated at upper method scope limit**



# ISO 4259



## ISO 4259

### Example of construction of specification limits

Sulfur in automotive fuels by WDXRF - EN ISO 20884:2011 (low range)

- $R = 0,1201 X + 1,9$       Working range: 5 - 60 mg/kg
- Scope of the test method: 4,5 - 60 mg/kg
- Lowest acceptable single result: 1,6 mg/kg
- Lowest possible min specification limit: 4,5 mg/kg
- Highest possible max specification limit: 60 mg/kg
- According to the 2006 edition, the upper specification limit shall be not less than 5,0 mg/kg
  - $R(5,0) = 2,5$  (50%)

## ISO 4259

### Example of construction of specification limits

Sulfur in LPG by UVF - ASTM D6667-14

- $R = 2,3205 X^{0,7}$  Working range: 1 - 196 mg/kg
- Scope of the test method: 4,6 - 196 mg/kg
- Lowest acceptable single result: -3,5 mg/kg (!)
- Lowest possible min specification limit: 4,6 mg/kg (!)
- Highest possible max specification limit: 196 mg/kg
- According to the 2006 edition, the upper specification limit shall be not less than 166,7 mg/kg
  - $R(166,7) = 83,4$  (50%)

# ISO 4259

## ISO 4259-2:2017

### Assessment of quality conformance to specification and dispute procedure

Prerequisites for acceptance for laboratory test results:

- **Each laboratory's test result shall be obtained from a test method that is in statistical control in terms of precision and bias**, as substantiated by in-house SQC charts or other equivalent statistical techniques (see ASTM D6299)
- The **standard deviation from the control charts** (or equivalent statistical techniques), as calculated from at least 30 most recent results obtained over at least 15 days, with results that are separated by at least 6 h, **shall not exceed the published test method standard deviation (R / 2,77)**

# ISO 4259

## ISO 4259-2:2017

- **If evidence exists from the published results of multiple PTP, that the R for a published test method is statistically inconsistent with the R actually achieved, the latter may be used in lieu of the published R to judge conformance to this clause, provided all of the following conditions are met:**
  - if legally permissible
  - If the R calculated from multiple PTP have sufficient degrees of freedom (>30) using results that have been properly screened for outliers in accordance with GESD protocol in ISO 4259-1 or other equivalent statistical technique
  - upon mutual agreement between disputing parties

# ISO 4259

## ISO 4259-2:2017

- **Each laboratory shall be able to demonstrate, by way of results from participation in PTPs, if available, a sustained testing proficiency and a lack of bias relative to PTP averages for the appropriate test method(s).** In the event that suitable PTP is not available, proficiency shall be demonstrated by way of testing certified reference materials (CRM) and in-house control charts on quality control (QC) samples, or by other method validation techniques acceptable to both parties

## ISO 4259-2:2017

### Assessment of quality conformance by the supplier

- A **supplier** who has no other source of information on the true value of a characteristic than a **single result** shall consider, with **95 % confidence**, that the **product meets the specification limit**, only if the result,  $X$ , is such that:
  - in the case of a **single upper limit,  $A_1$** :  $X \leq A_1 - 0,59 R$
  - in the case of a **single lower limit,  $A_2$** :  $X \geq A_2 + 0,59 R$
  - in the case of a **double limit ( $A_1$  and  $A_2$ )**, both these conditions are **satisfied**

# ISO 4259

## ISO 4259-2:2017

### Assessment of quality conformance by the recipient

- A **recipient** who has no other source of information on the true value of a characteristic than a **single result** shall consider that the **product fails the specification limit with 95 % confidence**, only if the result,  $X$ , is such that:
  - in the case of a **single upper limit,  $A_1$** :  $X > A_1 + 0,59 R$
  - in the case of a **single lower limit,  $A_2$** :  $X < A_2 - 0,59 R$
  - in the case of a **double limit ( $A_1$  and  $A_2$ )**, either of these conditions applies



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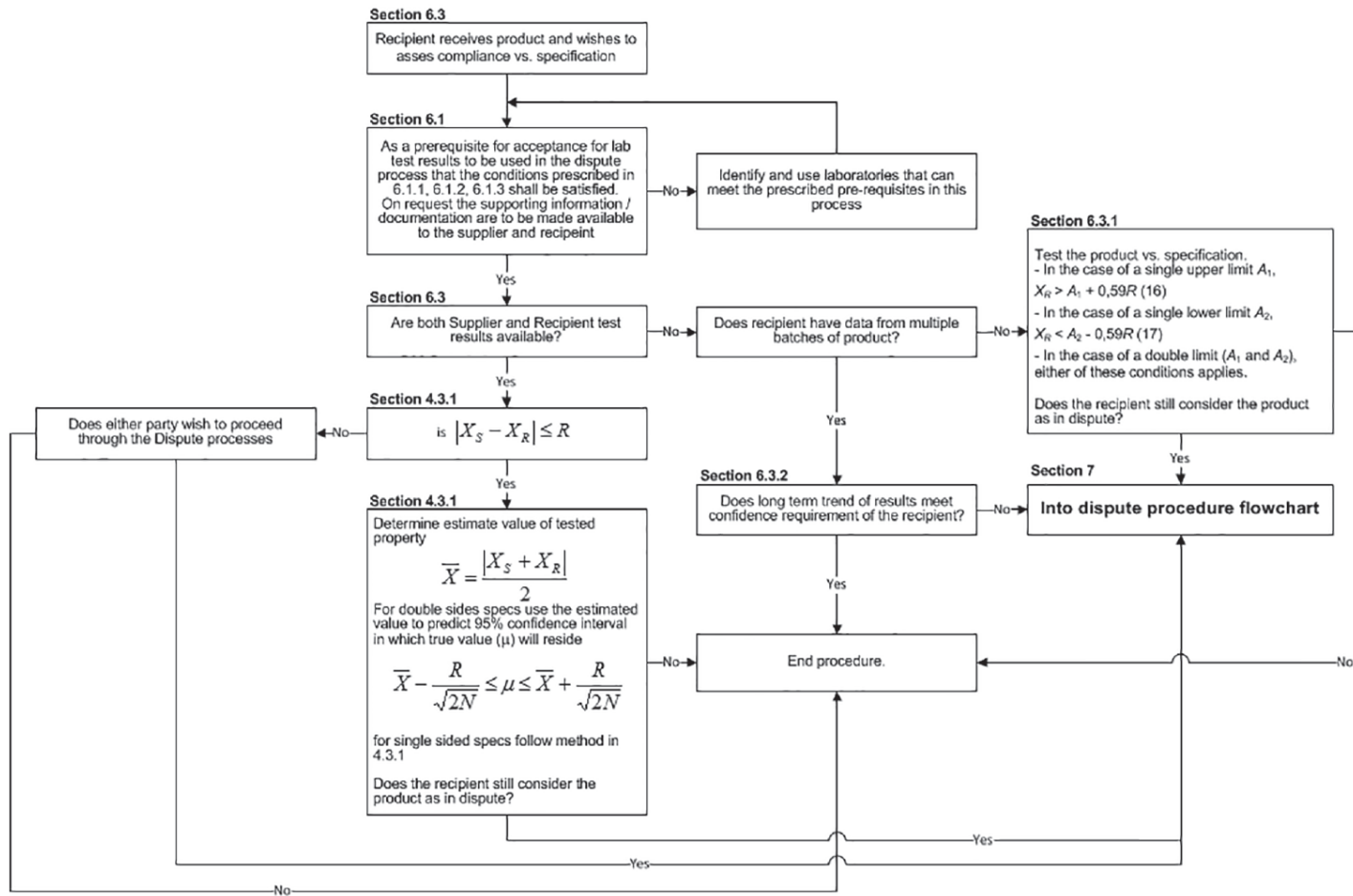


Figure 2 — Flowchart for assessment of specification conformance by recipient

# ISO 4259

## ISO 4259-2:2017

### Dispute procedure

#### Resolve dispute by negotiation

- Given the **complexity of the procedure**, it is **highly recommended that supplier and recipient attempt to resolve the dispute through negotiation** to arrive at mutually acceptable terms for settlement
- In order to engage in this procedure a **pre-requisite** is that there is a **sufficient amount of agreed-upon adjudication sample available**

# ISO 4259

## ISO 4259-2:2017

### Use of the test method or procedure in case of dispute

- **For a specification document that lists multiple test methods for the same property, or, a test method standard where multiple procedures for the same property are given, the designated referee method or procedure shall be given**
- It is the responsibility of the standardization committee supervising either the specification or the test method standard to ensure a referee method or procedure for adjudication purposes is designated in the document
- **In the event that a referee method or procedure is not specified, supplier and receiver shall agree on a specific method or procedure prior to execution of the dispute procedure**

# ISO 4259

## ISO 4259-2:2017

### Dispute resolution procedure

- **If the supplier and the recipient cannot reach agreement regarding the specification conformance for the quality of the product on the basis of their existing results, then the dispute resolution procedure shall be adopted.** If necessary, the degree of criticality,  $p_c$ , has to be agreed upon in advance between supplier and recipient
- **Each laboratory shall reject its original results and obtain at least three other acceptable results on their own check sample** to ensure that the work has been carried out correctly under repeatability conditions. **The average of the acceptable results in each laboratory shall then be computed**

# ISO 4259

## ISO 4259-2:2017

### Dispute resolution procedure

- **If the re-testing does not resolve the dispute, then:**

- If  $\frac{\bar{X}_S + \bar{X}_R}{2} \leq A_1$  or  $\geq A_2$

- Product meets the specification if  $|\bar{X}_S - \bar{X}_R| \leq 0,84R_2$

- It cannot be stated with confidence whether the product does or does not comply with the specification limit if  $|\bar{X}_S - \bar{X}_R| > 0,84R_2$

In this case resolution of the dispute may be achieved by negotiation

- If  $\frac{\bar{X}_S + \bar{X}_R}{2} > A_1$  or  $< A_2$  dispute whatever the difference  $\bar{X}_S - \bar{X}_R$

# ISO 4259

## ISO 4259-2:2017

### Dispute resolution procedure

- If  $|\bar{X}_S - \bar{X}_R| > 0,84R_2$  , and the dispute is unresolved, the two laboratories shall contact each other and compare their operating procedures and apparatus
- Following these investigations, a correlation test between the two laboratories shall be carried out on their check samples. The average of at least three acceptable results shall be computed, in each laboratory, and these averages compared as indicated in the previous step **REMOVED!**

## ISO 4259-2:2017

### Dispute resolution procedure

- If the disagreement on product conformance status still remains and resolution of the dispute cannot be reached by negotiation, **at least one additional third-party laboratory** that is neutral, expert and accepted by the two parties in dispute shall be invited to assist in the dispute resolution
- **All parties shall first agree on a common adjudication sample**
- Subject to sample volume adequacy, **each party shall obtain their own average to be used for adjudication purposes using at least three acceptable results for the adjudication sample.** If there is an insufficient amount of adjudication sample available, all parties shall agree to the number of test results that each party is to use to calculate their average to be used for adjudication purposes

## ISO 4259-2:2017

### Dispute resolution procedure

- If the difference between the most divergent laboratory adjudication result and the average of the two other laboratory adjudication results is less than or equal to  $R_3$ :

If  $\frac{\bar{X}_S + \bar{X}_R + \bar{X}_E}{3} \leq A_1$  or  $\geq A_2$ , product meets specification.

If  $\frac{\bar{X}_S + \bar{X}_R + \bar{X}_E}{3} > A_1$  or  $< A_2$ , product fails specification.



## ISO 4259-2:2017

### Dispute resolution procedure

- If the difference between the most divergent laboratory adjudication result and the average,  $\bar{X}$ , of the other adjudication results is more than  $R_3$ :

If  $\bar{X} \leq A_1$  or  $\geq A_2$ , product meets specification.

If  $\bar{X} > A_1$  or  $< A_2$ , product fails specification.

- If more than one additional third-party laboratory is involved...

# ISO 4259

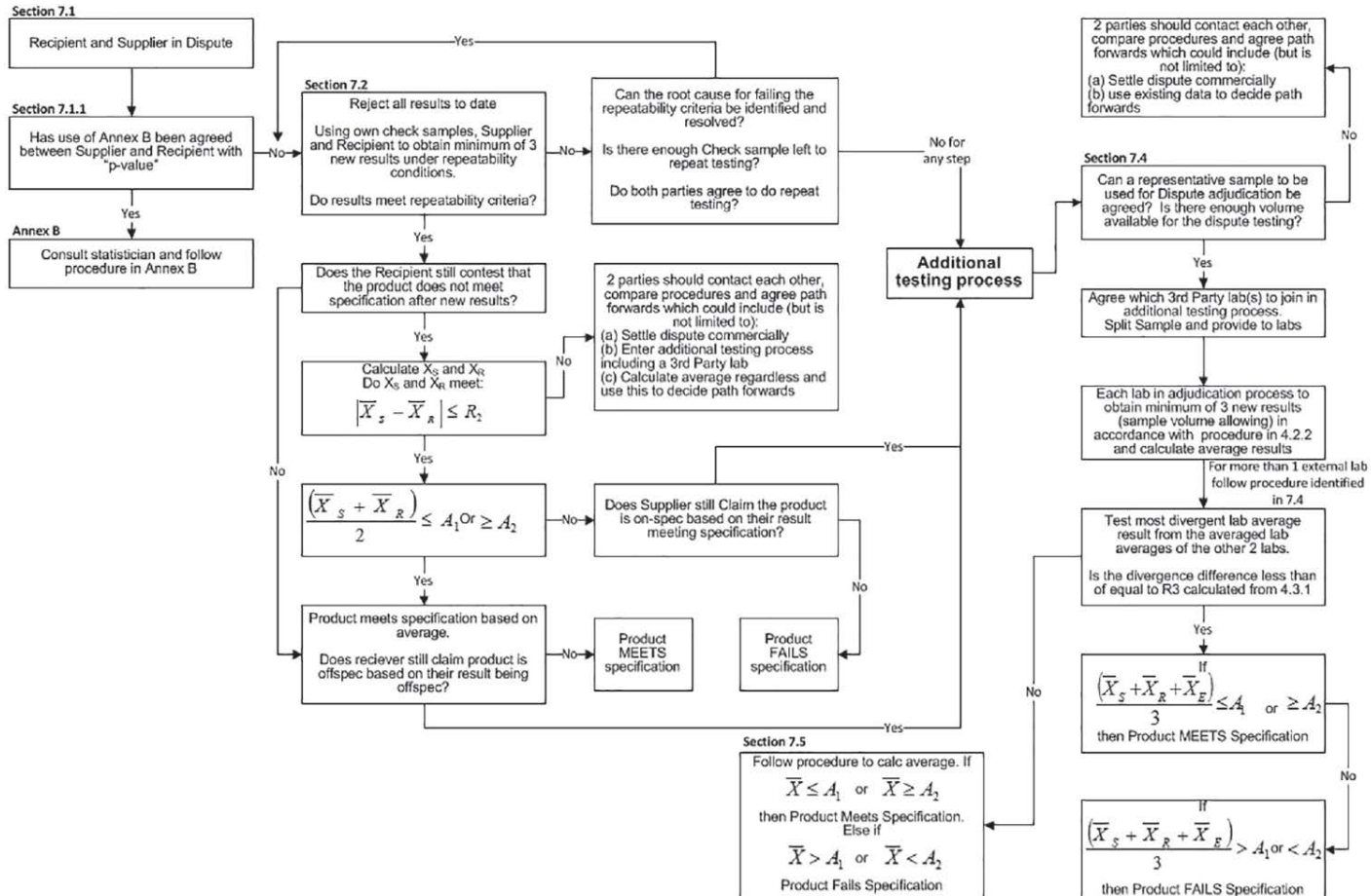


Figure 3 — Flowchart for dispute procedure

# ISO 4259

## Next steps

- **ISO/CD 4259-3**, *Petroleum products - Precision of measurement methods and results - Part 3: Monitoring and management of precision data in relation to methods of test*
- **Bias assessment?** See ASTM D6708, *Standard Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material*

Per ulteriori informazioni

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